

## **Experimental Determination of Oxygen-isotope Fractionations Between CO<sub>2</sub> Vapour and Soda-melilite Melt**

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Oxygen-isotope measurements of igneous rocks and minerals can constrain their origin and evolution, but they are interpretable only in light of known  $^{18}\text{O}/^{16}\text{O}$  fractionations among co-existing silicate melt, minerals, and magmatic volatiles. There have been many experimental studies of mineral-mineral and mineral-fluid fractionations but few involving silicate melt, particularly basic and ultrabasic melts relevant to study of mantle geochemistry and basaltic volcanism (Muehlenbachs & Kushiro, 1974). Consequently, fractionations involving such melts are generally estimated based on the systematics of differences in  $\delta^{18}\text{O}$  between phenocrysts and co-existing glass or groundmass. Estimates of this type, although useful, are insufficient for interpreting the usually subtle oxygen isotope variations observed in many basaltic suites. Therefore, we have undertaken a series of experiments examining oxygen-isotope fractionations involving basic silicate melts. We report here measurements of fractionations between the CO<sub>2</sub> and soda-melilite melt. This composition has been used previously as an analog for basic silicate melts.

We report here the results of experiments at 1250±10 C and 1400±10 C on exchange of oxygen isotopes between CO<sub>2</sub> vapor and Na-rich (Na<sub>2</sub>O of 12 wt%) melt corresponding to a mineral end member with melilite stoichiometry. All experiments were performed at 1 bar total pressure in a vertical Deltech(r) tube furnace by suspending glass chips (0.5-1 mm diameter) on Pt-wires and purging the furnace with a stream of CO<sub>2</sub> vapor with a known  $^{18}\text{O}$  value. Samples were suspended in the CO<sub>2</sub> gas for 4-48 h at 1250 C or for 7 h at 1400 C and then quenched to glass at room temperature. Na-loss occurred from the melt during experiments; final Na<sub>2</sub>O contents of samples ranged from 8.7 to 12.0 wt%. 'Reversals' were achieved by conducting experiments simultaneously on several different glass chips having similar major-element compositions but a range of initial  $\delta^{18}\text{O}$  values ranging from above and to below the value achieved at the end of a given experiment. Samples of the gas were collected at several times over the course of each experiment. Isotopic compositions of gas and oxygen released from glass run products (extracted by laser

fluorination) were measured on a Finnigan Mat 251 gas-source isotope-ratio mass spectrometer with a reproducibility of 0.05%.

Results of experiments at 1250 C are plotted in figure 1 as the measured difference in  $\delta^{18}\text{O}$  between CO<sub>2</sub> gas and quenched glass [ $\Delta(\text{CO}_2\text{-glass})$ ] as a function of the duration of the experiment. Starting glasses having a large range in  $\delta^{18}\text{O}$  values (both higher and lower than that of CO<sub>2</sub> gas) converge to a common and time-invariant value for  $\Delta(\text{CO}_2\text{-glass})$  of  $2.7\pm0.3\text{‰}$  ( $\pm 2\sigma$ ) within ~ 1 day. We interpret this value to be the equilibrium fractionation between CO<sub>2</sub> and Na-rich melilite melt. After 7h at 1400 C, a  $\Delta(\text{CO}_2\text{-glass})$  value of  $2.2\pm0.2\text{‰}$  ( $2\sigma$ ) is achieved. Results can be described by the relationship:  $1000\ln\alpha = A * 10^6 T^{-2}$ , where A equals  $6.2\pm0.6$  ( $\pm 2\sigma$ ).

Differences between our results for fractionations between CO<sub>2</sub> and Na-rich melilite and those previously measured between CO<sub>2</sub> and rhyolite melt (Stolper & Epstein, 1991) and between CO<sub>2</sub> and albite/anorthite melt (e.g. Matthews et al., 1994) are consistent with the effects of melt composition estimated using the Garlick index (Garlick, 1966; Matthews et al., 1994). Such calculations suggest also that the Na-rich melilitic composition would be a good analog for natural olivine tholeiites in terms of their oxygen-isotope partitioning. Using our results and extrapolate the results of Matthews et al. (e.g. 1994), we calculate an oxygen fractionation between plagioclase and soda-melilite melt of 0.1-0.5‰ at 1250 C which is similar to the results measured by Muehlenbachs & Kushiro (1974) on basaltic system. Combining our results with previous determinations of fractionations between calcite and olivine and between CO<sub>2</sub> and calcite suggest that oxygen isotope fractionations between basaltic melt and olivine are ~0.6-1‰ at 1300 C (albeit with a large accumulated uncertainty). This estimate is within errors of that estimated based on calculations using the Garlick index (Matthews et al., 1994) and within the range of values measured for phenocryst-matrix partitioning in terrestrial and lunar basalts (e.g. Clayton et al., 1971; McPherson & Matthey, 1998; Eiler et al., 2000).